SELECTIVE DIALKYLATION OF NAPHTHALENE WITH HINDERED ALKYLATING AGENTS OVER HM AND HY ZEOLITES UNDER LIQUID PHASE CONDITIONS.

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INTRODUCTION

Whereas the use of zeolite catalysts has been widely investigated for the shape-selective conversions of mononuclear aromatic hydrocarbons, such as alkylation of toluene or isomerization of xylenes[1-3], in contrast relatively few reports are available on the conversion of polynuclear aromatics, such as naphthalene derivatives. Among the latter, 2,6-dialkylnaphthalenes are the most valuable compounds, since, as precursors of 2,6-naphthalene dicarboxylic acid, they are potentially useful raw materials for production of high quality polyester fibers and plastics[4] and of thermotropic liquid crystal polymers[5].

The interest of such derivatives was shown, in the recent years, by the increasing number of patents relevant to their preparation and separation. Following the pionneering work of Fraenkel et al.[6] on the alkylation of naphthalene with methanol over various zeolites, much attention has been paid, in the early nineties, to studies on the activity and selectivity of zeolites in the isopropylation of naphthalene[7-9]. The interest of the use of bulky substituents in such reactions over zeolites has been clearly demonstrated by recent papers[10-12].

The present communication is concerned with the results obtained in the alkylation of naphthalene over a series of HM and HY zeolites, using isopropyl bromide, cyclohexyl bromide and cyclohexene as alkylating agents, under liquid-phase conditions, leading to a better regulation of the reaction pathway.

EXPERIMENTAL

Materials. Analytical grade cyclohexane, isopropyl bromide, cyclohexyl bromide, cyclohexene and naphthalene (Aldrich Chemical) were used as supplied.

Catalysts. H mordenite (Zeolon 100-H, Si/Al = 6.9 from Norton) and three dealuminated mordenites were used for the isopropylation reactions. The dealuminated mordenites were prepared, according the published procedure[13], from Zeolon 100-H (HM) by treatment in 1M HCl solution at 100°C for 3 h or refluxing in 3 M HCl solution for 6 h or in 6 M HCl solution for 12 h. The resulting powders, washed and oven dried at 110°C, had Si/Al atomic ratios of 9 (HM1), 13.1 (HM2), and 20.6 (HM3). The HY catalyst was derived from the thermal decomposition of NH4Y (Linde SK 41, Si/Al = 2.5 from Union Carbide). The US-HY was supplied by Chemisch Fabrik Uetikon, Zürich (Z6-05-01, Si/Al = 2.5). The CVD-modified zeolites were obtained according the silanation procedure[9], and fully characterized by various technics[14].

For the cyclohexylation reactions, the US-HY used was the same as above. The dealuminated HY (Si/Al = 19.5) and HM (Si/Al = 10.8) were from Zeocat, Montoir de Bretagne (ZF 520 and ZM 510).

Catalytic runs. The isopropylation of naphthalene was carried out in a 0.1 liter stirred autoclave reactor (Sotelem). In a typical run, the autoclave was charged with 1 g of zeolite freshly calcined in air at 500°C, a mixture of 5 mmol naphthalene and 10 mmol isopropyl bromide in 50 ml of cyclohexane and heated to 200°C. Samples were withdrawn periodically and analyzed by GLC (Altech OV1 capillary column, 10 m or 25 m x 0.25mm).

The same procedure and analysis technic were used for cyclohexylation reactions with cyclohexyl bromide. When cyclohexene was used, the procedure was the following: the autoclave was charged with naphthalene (5 mmol), cyclohexane (50 ml) and the catalyst (1 g), and heating was started; cyclohexene (10 mmol) was then added, drop by drop, by means of a stainless steel pressurized funnel, and the

mixture was stirred in the same conditions as above.

For the isolation and purification of 2,6-dicyclohexylnaphthalene, the procedure was the following: after cooling, the catalyst was filtered and cyclohexane evaporated; the crude product solidified at room temperature, the solid was then filtered and recrystallized from ethanol (mp 152°C after two recrystallizations). The structure was confirmed by GC-MS, ^{1}H and ^{13}C NMR spectroscopy together with X-ray crystallography[15].

RESULTS AND DISCUSSION

Isopropylation reaction over HM and HY zeolites. The isopropylation of naphthalene with isopropyl bromide over a series of mordenites and Y zeolites show that both conversion and selectivity depend largely upon the nature and the structure of the catalyst. The main results, obtained in this study and reported in Table 1, can be summarized as follows:
- mordenites are less active than Y zeolites;
- in both cases, a high β-selectivity is found, leading to the selective formation of 2-isopropylnaphthalene and a mixture of 2,6- + 2,7-diisopropylnaphthalenes;
- the formation of trialkylnaphthalenes cannot be avoided over untreated zeolites.

The origin of the high β-selectivity observed is different depending on the zeolite. Over H-mordenites, such a selectivity is explained as the result of transition-state shape selectivity, due to the constrained environment in the channels of the mordenite; the steric hindrance of the 1-isopropylnaphthalene (α-isomer) does not allow its formation inside the tight one-dimensional tunnels of the zeolite. Over Y zeolites, the β-selectivity has been shown to be due to a thermodynamic equilibrium favorable to the 2-isopropylnaphthalene; the 1-isopropylnaphthalene (kinetic product) is initially formed inside the three-dimensional large-pore structure of Y zeolites, and it is then rearranged into the 2-isomer (thermodynamic product) at high temperatures.

Over the two kinds of zeolites, 2,6- and 2,7-diisopropylnaphthalenes are the main disubstituted derivatives. Such a result is expected taking into account the β-selectivity observed in the monoisopropylation step, whatever the origin of this selectivity.

In both cases, in our experimental conditions, the same distribution between the 2,6- and 2,7- isomers (2,6-/2,7- ratio = 1) is observed; such a result seems not surprising, if we consider that these two isomers have the same kinetic diameter (6.5Å), and that their production and subsequent diffusion in the pores or cavities of zeolites occur in the same way. Nevertheless, a higher 2,6-/2,7- ratio is generally observed over mordenites by some authors[7,8,10]; various assumptions, such as differences in diffusion rates or in the ease of transition-state formation for the two isomers, might explain these higher ratios, obtained in different experimental conditions.

These results are very encouraging regarding the efficiency of the catalytic activity of zeolites in isopropylation of naphthalene and their shape selectivity properties. Nevertheless, the selective formation of the 2,6-isomer is not possible in any case. The possibility of an improvement of such a selectivity has then been considered by the use of either modified zeolites or more hindered alkylating agents.

Isopropylation over CVD-modified zeolites. Shape-selectivity of zeolites may be improved by reducing the number of active sites of the external surface. It is known that silanation of zeolites leads not only to such a deactivation of the outer active sites but also to a uniform control of the pore-opening size of the zeolite[16,17]. The "chemical vapor deposition" silanation method[18] leads, in particular, to a remarkable enhancement of the reactant and product shape-selectivity[19,20].

Over such CVD-modified zeolites, the formation of the bulky trialkylnaphthalenes is totally suppressed in the case of mordenites, and considerably reduced with the HY zeolites (2% compared with 14% over the untreated zeolite) (Table 1). Such a result clearly demontrates that the trialkylation reaction occurs on the acidic sites located on the external surface of mordenites. The acidic outer sites of the HY zeolites are also largely involved in the formation of the triisopropyl derivatives, which can be, nevertheless, produced also inside the cavities of these three-dimensional large-pore Y zeolites.

The results obtained in the isopropylation of the 2-isopropylnaphthalene over CVD-modified HY zeolite, i.e. a drastic decrease in the amount of triisopropylnaphthalenes (4% instead of 18% over the untreated HY), leading to an

enhancement of the β-selectivity over the CVD-modified HY for this reaction (85%), confirm such an involvement.

With CVD-modified HM, the 2-isopropylnaphthalene is the major product (90% at 10% conversion); despite the low conversion, this result must be taken into account because 2-isopropylnaphthalene can be easily separated from the reaction mixture by simple distillation, and then isopropylated as starting material for diisopropylnaphthalene production. With CVD-modified HY zeolites, a high β-selectivity (>90%) is obtained, corresponding to 63% of 2-isopropylnaphthalene and 30% of 2,6- + 2,7-diisopropylnaphthalenes at 70% conversion.

The overall results show that, from a synthetic point of view, the CVD-modified zeolites appear to be the best catalysts with which it is possible to selectively obtain β- and ββ'- isomers.

Cyclohexylation reaction over HY zeolites. As already said above, no selectivity in 2,6-diisopropylnaphthalene could be found despite the hindrance of the isopropyl group; moreover, the separation of 2,6- and 2,7-diisopropyl isomers is very difficult. It was reported that, in the cyclohexylation reaction of naphthalene under conventional conditions (i.e. over Friedel-Crafts catalysts, such as aluminum chloride), the 2,6-dicyclohexylnaphthalene could be isolated, in a very low yield, from the reaction mixture by crystallization[21,22].

Taking into account such a property and the steric hindrance of the cyclohexyl group, we studied the catalytic activities of a sample of H-mordenite and two samples of HY zeolites in the cyclohexylation reaction of naphthalene with cyclohexyl bromide and cyclohexene respectively (Table 2).

The H-mordenite presents a weak activity in the reaction with the cyclohexyl bromide, as shown by the low conversion of naphthalene (6%) at 200°C, whereas the HY zeolites appear to be very efficient even at lower temperatures. The ultrastable zeolite HY (Si/Al = 2.5) and the dealuminated sample (Si/Al = 20) exhibit similar activity and selectivities at the same temperatures, as shown on Table 2. When cyclohexene is used as the alkylating agent instead of cyclohexyl bromide, a slight difference is observed if the reaction is carried out under the same conditions (naphthalene and alkylating agent put together in the autoclave), due to dimerisation of cyclohexene. When cyclohexene is added drop by drop to the stirred mixture, the same results are then obtained, both in conversion and selectivity.

The comparison of cyclohexylation with isopropylation of naphthalene over the ultrastable zeolite US-HY under the same conditions is given on Table 3. In both reactions, a high conversion of naphthalene is obtained after short reaction times (10 min with cyclohexyl bromide, 1 h with isopropyl bromide).

The cyclohexylation reaction yields an increasing amount of 2,6- and 2,7-dicyclohexylnaphthalenes, together with a significant decreasing amount of trialkyl derivatives due to the steric hindrance of the cyclohexyl group, leading to an improvement of the β-β' selectivity (82% compared with 71%). Nevertheless, the relative distribution of the 2,6- and 2,7- isomers does not dramatically change (2,6-/2,7- = 0.95 for isopropyl and 1.1 for cyclohexyl. Such a result confirms that Y zeolites increase the ββ' selectivity, but do not lead to the predominant formation of one given dialkyl isomer.

The advantage of the cyclohexylation in comparison with the isopropylation is directly related to the physical properties of the 2,6-dicyclohexylnaphthalene, which is separated from the mixture by crystallization.

Pure 2,6-dicyclohexylnaphthalene (white crystals, mp = 152°C) is isolated in moderate yields (19 to 27%) depending on the zeolites[23].
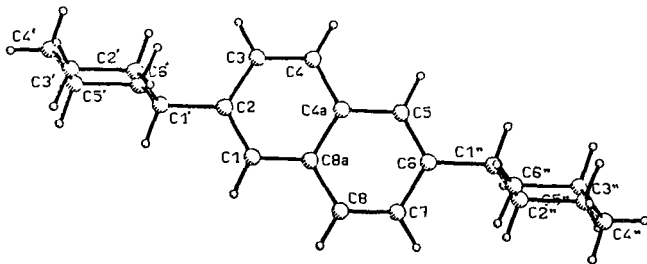
As shown above, this crystalline 2,6-dicyclohexylnaphthalene contains a crystallographic symmetry centre; the cyclohexyl substituents adopt a chair conformation, and the presence of the two bulky substituents involves only a slight deviation from flatness for the naphthalene ring[15].

CONCLUSION

The liquid-phase alkylation of naphthalene with hindered alkylating agents such as isopropyl and cyclohexyl derivatives can be carried out efficiently over HM and HY zeolites. High conversions and efficient β-β' selectivities are obtained after very short reaction times at 200°C. In the case of isopropylation with isopropyl bromide, the use of zeolites modified by silanation of the external surface leads to an improvement of such a selectivity by suppressing or reducing the formation of the triisopropyl derivatives. The use of cyclohexyl derivatives, cyclohexyl bromide or cyclohexene, as alkylating agents, yields, over HY zeolites, an increasing amount of 2,6- and 2,7-dicyclohexylnaphthalenes, together with a significant decreasing of the trialkyl derivatives. Moreover, the 2,6-dicyclohexylnaphthalene, a crystalline compound, is easily separated from the reaction mixture by crystallization, which is, to our knowledge, the first exemple of the production of a pure 2,6-dialkylnaphthalene.

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Table 1. Isopropylation of Naphtalene over a Series of Untreated and CVD
Modified Zeolites at 200°C with Isopropyl bromide

Catalyst	time, h	naphth. conv., %	product distribution, %					selectivity, %	
			MIPN 2-IPN	DIPN 2,6-	DIPN 2,7-	DIPN others	TIPN	2,6- +2,7- DiPN	overall β-select.
HM	24	18	81	4	4	3	8	72	89
HM$_1$	24	60	74	7	6	5	10	70	87
HM$_2$	24	20	61	13	11	9	9	74	85
HM$_3$	24	16	55	14	13	7	9	80	82
HY	1	86	42	16	17	12	14	73	74
US–HY	1	97	28	19	20	16	17	71	67
CVD-HM	1	10	90	3	4	3	0	70	97
CVD-HY	1	70	63	15	15	5	2	85	93

Table 2. Cyclohexylation of Naphtalene over Zeolites at 200° C with
Cyclohexyl bromide (CB) and Cyclohexene (CH)

Catalyst	Alkylat. agent	time, min	naphth. conv., %	product distribution, %			selectivity ,%		
				MCN	DCN	TCN	2-MCN MCN	2,6-DCN DCN	2,6- +2,7- DCN DCN
HM	CB	70	6	56	44		46	16	27
HY$_{2.5}$	CB	10	96	31	67	2	6	43	82
HY$_{20}$	CB	10	94	53	46	1	8	43	79
	CH[a]	10	90	85	15		53	20	36
	CH[b]	25[c]	98	44	54	2	7	41	77

[a] CH charged together with naphthalene in the autoclave before heating. [b] CH added drop by drop. [c] time
corresponding to the end of addition of naphthalene.

Table 3. Isopropylation and Cyclohexylation of Naphtalene over US-HY Zeolite at 200°C
with Isopropyl bromide (IB) and Cyclohexyl bromide (CB)

Alkyl. agent	time min	naphth. conv.,%	product distribution, %						selectivity,%
			MAN[a]	DAN[b] 2,6-	2,7-	2,6- +2,7-	others	TAN[c]	2,6- +2,7-DAN DAN
IB	60	97	28	19	20	39	16	17	71
CB	10	96	31	29	26	55	12	2	82

[a] MAN : monoalkylnaphthalenes. [b] DAN : dialkylnaphthalenes. [c] TAN : trialkylnaphthalenes.